

Formation of crystalline dots and lines in lanthanum borogermanate glass by the low pulse repetition rate femtosecond laser

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ABSTRACT

Femtosecond lasers have become a powerful tool for 3D space-selective crystallization of glasses. A laser-induced cumulative heating effect required for crystal growth is usually considered to take place only at pulse repetition rate over 100 or 200 kHz and 200 kHz is known as the lowest repetition rate at which femtosecond laser-induced crystallization has been reported so far. We for the first time demonstrate precipitation of LaBGeO₅ crystals in lanthanum borogermanate glass using a femtosecond laser emitting 1030 nm, 300 fs, 110 μJ pulses with adjustable repetition rate below 100 kHz. For the applied laser, minimal repetition rate enabling nucleation of ferroelectric LaBGeO₅ crystals inside the glass was shown to be 9 kHz at maximal pulse energy of 110 μJ and growth of a crystalline line from the formed seed crystal was obtained starting from 8 kHz though smooth homogeneous oriented line which might be regarded as quasi-single-crystalline could be grown at 25 kHz or higher and corresponding pulse energy of 18 μJ. Thus, the pulse repetition rate sufficient for a cumulative heating effect and a stable crystal growth was reduced by an order of magnitude as compared to earlier publications due to relatively high pulse energy. Possibility and efficiency of cumulative heating and crystal growth and average time required for forming the seed crystal have been studied for various combinations of the pulse energy and the repetition rate. Obtained crystalline features have been studied by micro-Raman spectroscopy and Raman mapping which confirmed growth of stillwellite-like LaBGeO₅ phase and orientation of its polar axis along the direction of the crystalline line.

Keywords: femtosecond laser, microstructure fabrication, space-selective crystallization, cumulative heating, lanthanum borogermanate glass, LaBGeO₅

1. INTRODUCTION

Space-selective processing of dielectrics by means of ultrafast lasers is an efficient tool for high-precision 3-dimensional microfabrication of integrated waveguides, microfluidics, optical storage etc.^[1]. The main advantage of the femtosecond laser pulses is extremely high peak power which under condition of tight focusing provides light intensity about 10¹⁴ W/cm² launching multiphoton absorption and subsequent avalanche ionization. This results in good confinement of light-matter region even along the beam since this nonlinear absorption effect takes place only around the beam waist where sufficient light intensity is achieved. An athermal character of ultrashort pulse impact in the case of low pulse repetition rate also is an advantage since avoids heating and thermal dissipation of energy outside the light-matter interaction area and thus keeps high confinement of the modified region near the diffraction limit or even beyond it^[1,2]. It also makes femtosecond laser processing independent from laser wavelength. Linear absorption at the basic wavelength of the laser beam is undesirable but this condition is satisfied for most of transparent dielectrics including glasses. Still, there are some applications which require laser-induced heating. One of them is space-selective crystallization of glasses for fabrication of different crystal-in-glass architectures (dots, arrays, straight or curved lines as prototypes of waveguides) which are especially interesting if crystals possess some functional properties such as a strong optical nonlinearity or a specific luminescent activity. They are regarded as a fundament for a new generation of components for optical frequency conversion, electrooptical modulation and switching as well as laser amplification or generation in integrated optical circuits with numerous functional elements fabricated in a single piece of glass. However crystal growth is a relatively slow process which requires long heat-treatment as compared to duration of single femtosecond pulses.

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Continuous-wave lasers are suitable for space-selective heating but enable mainly surface crystallization and, moreover, only in glasses possessing significant absorption at the laser wavelength which is usually realized through introduction of some light absorbing additives, e.g. rare-earth or transition metal ions^[3,4].

Appearance of femtosecond regenerative amplifiers with a pulse energy of about microjoules and a pulse repetition rate enabled cumulative heating effect which is provided when heat generated in the matter by a single pulse has no time to be fully dissipated before coming of the next pulse. That opened up an opportunity of three-dimensional space-selective precipitation of functional crystals in the inside of the glass which has been already demonstrated in several glasses^[5-15] including BaB₂O₄ in a barium aluminoborate glass^[5], BaTiO₃ and BaTi₂Si₂O₈ in barium titanosilicate and sodium barium silicate glasses^[6-8], Sr₂TiSi₂O₈ in strontium titanosilicate glasses^[9], LiNbO₃ in lithium niobosilicate glasses^[6,10,11], Dy₂(MoO₄)₃ in a dysprosium molybdenum borate glass^[12]. A common feature of all those works is a pulse repetition rate of the applied lasers as large as 200-250 kHz or even higher. Studies of the cumulative heating effect and laser-induced temperature distribution in different oxide glasses^[11, 13-15] demonstrated that 200 kHz is an approximate threshold for femtosecond laser-induced crystallization of oxide glasses. Still, all this studies were performed using laser systems with similar pulse energy.

A number of important studies on femtosecond laser-induced crystallization was performed for a lanthanum borogermanate glass^[16-19]. A ferroelectric lanthanum borogermanate LaBGeO₅ possessing stillwellite-like structure is one of the favorite objects for studies in the field of functional materials based on glass crystallization since it has a chemical composition located in the glass-forming region of La₂O₃-B₂O₃-GeO₂ (LBG) ternary system enabling precipitation of the crystal from glasses with chemical composition around LaBGeO₅ as a single phase in the glass. LaBGeO₅ crystal combines ferroelectric properties and second harmonic generation activity with possibility for partial or full replacement of La by some rare earth elements (Nd, Pr, Sm etc.) keeping stillwellite-like structure and optical nonlinear properties of the crystal^[20,21]. For instance, laser generation at ⁴F_{3/2}←⁴I_{11/2} transition of Nd³⁺ was obtained for Nd-doped LaBGeO₅ both in glassy (1068 nm) and crystalline (1048 nm) state^[22,23], the latter material being regarded as a promising active media for lasers with self-frequency doubling. LaBGeO₅ crystal can be precipitated both at the surface and in the bulk of the LBG glass enabling fabrication of high-quality pyroelectric textures, transparent surface nonlinear crystalline layers or bulk nanostructures^[24-27]. Space-selective techniques using continuous-wave or pulsed lasers enabled obtaining surface crystalline LaBGeO₅ or (La, Ln)BGeO₅ structures such as quasi-single-crystal continuous lines^[28] or accumulations of separate microcrystals^[29-31] were obtained. To initiate laser beam absorption and laser heating, Sm³⁺^[28,31], Nd³⁺^[29,31] or Cr³⁺^[30] ions were introduced depending on the applied laser wavelength. The LBG glass was also the first object for demonstration of femtosecond laser writing of three dimensional curved crystalline lines in the inside the glass with orientation of the polar axis corresponding to the direction of the line including curved intervals^[16]. Effect of the distance from the glass surface on the shape of the femtosecond laser-written crystalline line cross-section^[17] and its correction through modification of the laser beam^[19] were also shown on the LBG glass.

In this work, we chose this favorable object to study a possibility of the laser-induced crystallization in the pulse repetition rate region of 100 kHz and lower which had been previously regarded as unsuitable for cumulative heating effect and ultrafast laser-induced precipitation of crystals in oxide glasses.

2. EXPERIMENTAL

2.1. Fabrication of glass samples

The glass under investigation had 25La₂O₃·25B₂O₃·50GeO₂ molar composition which exactly corresponded to that of LaBGeO₅ crystal. Chemically pure La(OH)₃, H₃BO₃ and GeO₂ were used as starting reagents for preparing a batch. Glasses were prepared using a conventional melt-quenching technique. The reagents were thoroughly mixed together and molten at 1300°C for 30 min in a platinum crucible placed into an electric furnace. To compensate boron oxide evaporation during melting, we used a platinum cover and compacted batch. The melt was poured on a steel plate and quenched by pressing with another plate to 3 mm thickness. The as-quenched glass was annealed for 2 hours at 630°C (i.e. ~40°C below glass transition temperature T_g of LBG glass^[27]) and slowly cooled down to a room temperature. Then it was cut into plane-parallel samples with thickness of approximately 1 mm. Special attention was paid to thorough mirror-grade polishing of the samples with diamond suspension since it is required to avoid surface scattering and distortion of the laser beam.

2.2. Laser experiments

The experimental setup for direct laser writing is shown in Fig.1. We used TETA Yb regenerative femtosecond amplifier (Avesta Ltd.) emitting pulses with duration of 300 fs at the wavelength of 1030 nm and a pulse repetition rate up to 100 kHz. The output collimated beam is a nearly symmetric Gaussian with $M^2 < 1.3$. A pulse energy was equal to 50 μJ at 100 kHz repetition rate but could be increased up to 100 μJ at 50 kHz or to 110 μJ at most at 25 kHz. External triggering with a signal generator was used to vary the pulse repetition rate gradually whereas an electrooptical attenuator enabled gradual reducing the pulse energy to 1 μJ .

The laser beam was focused inside the sample through OLYMPUS LCPLN-IR, 50X objective (N.A. = 0.65) with near-IR-optimized transmittance. The objective can be moved vertically with a computer-controlled high-precision motor. A camera was used to obtain a live view of the laser exposure process which was important for revealing time of crystal growth and a real-time inspection of the structures being written by the beam inside the glass. A sample was placed on a motorized two-axis translation stage moving in a horizontal plane and controlled by the computer which provided variation of translation speed and contour.

In this study, we tried to obtain crystalline dots and lines at various beam parameters and scanning speed. Crystal dots were produced by the stationary laser beam. Possibility and efficiency of crystal growth and average time required for forming a microcrystal by the stationary laser beam have been studied for various combinations of the pulse energy and the repetition rate. All the data given below were obtained for the beam was focused at a depth of 100 μm below the surface. Crystalline lines were grown from the seed crystal, by scanning the glass sample with the laser beam at the selected speed. All these experiments were performed at room temperature.

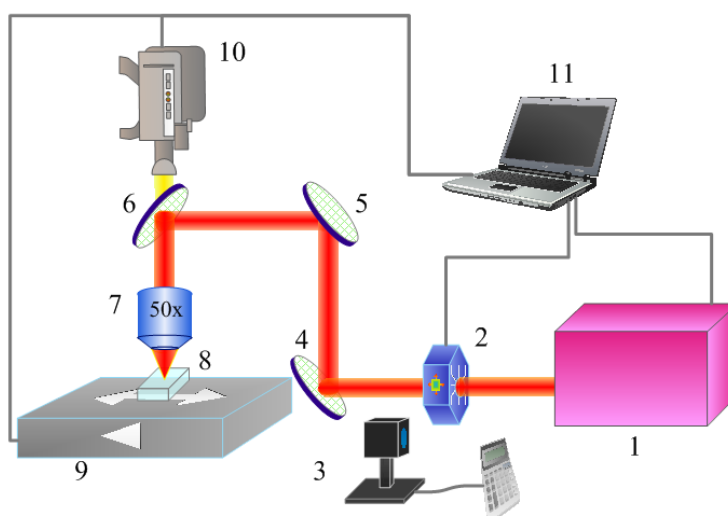


Figure 1. Experimental setup: 1 - laser source, 2 - attenuator, 3 - power meter, 4,5,6 - mirrors, 7 - microscope objective, 8 - sample, 9 - motorized translation two-axis stage, 10 - camera, 11 - computer.

2.3. Analysis of laser-induced structures in the glass

Real-time detection of crystallization under the laser beam was performed thanks to second harmonic generation activity of the precipitated LaBGeO_5 phase. Once a crystal appeared, distinct green glow appeared due to second harmonic generation (SHG) response whereas only white light was emitted from the glass region being in focus if crystallization didn't take place. Thus the presence of the crystalline phase were determined immediately during laser treatment through the green glow which could be directly observed in a real-time image transmitted from the camera to the computer and on demand recorded. Morphology of space-selectively grown crystalline patterns was studied using Olympus BX-51 polarizing optical microscope. The morphology of the crystal lines was observed with polarization optical microscopy. The crystal phase in glass samples were identified by means of micro-Raman spectroscopy. Polarized Raman spectra were recorded using a confocal micro-Raman spectrometer from NTEGRA Spectra nanolaboratory (NT-MDT Co.). As excitation source an argon ion laser with a wavelength of 488 nm was used. Raman signal was collected in back-scattering configuration. Laser beam diameter at the focus was about 2 μm . Polarization of the exciting beam could be changed with a half-wave plate. 2D Raman mapping was used to check shape and size of crystallized patterns.

3. RESULTS AND DISCUSSION

3.1. Formation of crystalline dots

At maximal available pulse repetition rate (100 kHz), 7-20 μm sized crystals could be formed by the stationary laser beam with average power of 0.4 - 1.82 W or, in other words, pulse energy ranging from 4 μJ to 18 μJ . Typically, some time passed before SHG response indicating appearance of a microcrystal could be observed but after SHG process was launched a crystal grew to its maximal size in about 1-2 s. This waiting time had a certain dispersion and average time drastically varied with the laser power. At constant repetition rate of 100 kHz, it was constant for the power range from 1.1 W to 1.85 W but reducing the laser power below 1.1 W resulted in considerable increase of waiting time up to several minutes as well as in increase of its dispersion (Fig. 2). For power lower than 0.4 W (i.e. pulse energy < 4 μJ) waiting time and time dispersion became too large to collect some data. Increasing the average power to 1.9 W or higher resulted in local destruction and cracking of the glass sample. The described order of events during the microcrystal formation is quite similar to that reported by A. Stone *et al.*^[18] for LBG glass but they examined dependence of waiting time on the focusing depth rather than on the laser power.

When keeping constant laser power, dependence of waiting time on pulse repetition rate was clearly inverse exponential. Thus at an average laser power of 1 W, waiting time at pulse repetition rate of 100 kHz was 100 times smaller than that at 30 kHz. Nevertheless we managed to reach the lower repetition rate boundary for laser-induced growth of microcrystals inside the glass equal to 9 kHz which is more than 20 times as low as ever reported so far^[11]. Maximal average power which could be achieved at 9 kHz was 1 W. Probably, if higher power was available, it could enable precipitation of microcrystals at even lower pulse repetition rate.

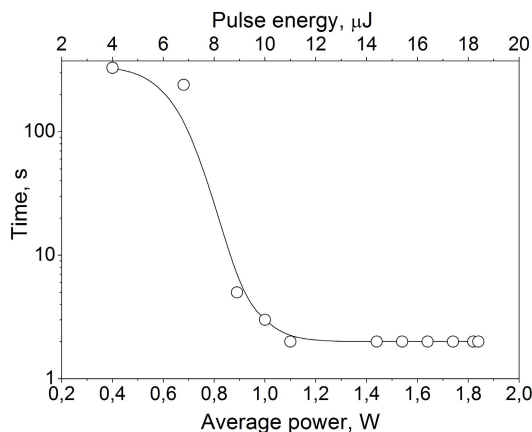


Figure 2. Average waiting time required to start crystal growth depending on the pulse energy / average power at constant pulse repetition rate of 100 kHz

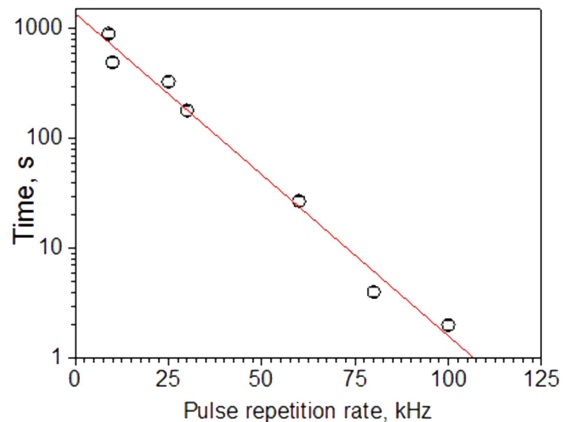


Figure 3. Average waiting time of crystal growth depending on the pulse repetition rate at constant average power ($P = 1$ W)

For the moment, we cannot suggest a detailed explanation of the dependences shown in Fig. 2, 3. Still, some assumptions can be done. According to constant waiting time for beam power above a some threshold (about 1.1 W at 100 kHz in our case), we can suggest that nucleation of the crystallite and growth up to size sufficient for noticeable SHG response takes a certain time equal to 2 s at the average for LBG at our conditions. Earlier studies^[11, 16-18] and our experiments allow us concluding that a crystallite giving rise to a microcrystal precipitates under the femtosecond laser beam at the interface between solid glass and glass melt. A large value of temperature gradient making a solid-liquid interface more pronounced is thought to be important for effective crystal nucleation. Reducing pulse repetition rate strongly diminishes cumulative heating effect and consequently the temperature gradient near the laser-exposed area. Nucleation of a crystallite is to some extent a stochastic process, its probability depending both on temperature and local glass structure, presence of inhomogeneities or defects. That explains a substantial dispersion of waiting time at the same irradiation conditions and increase of the dispersion with increase of waiting time.

3.2. Growth of crystalline lines

Laser-induced growth of crystalline lines included two stages. The first stage is the formation of a seed crystal. Typically it was a microcrystal grown by a stationary beam like in earlier studies^[16-19] but we also observed a possibility to grow a line from any point of another crystalline line formed earlier. The second stage is the crystal growing from the seed by

means of continuous scanning the glass with the focused laser beam. It should be emphasized that average power, pulse repetition rate and scanning speed ranges suitable for writing of a smooth homogeneous line are substantially narrower than those required just to grow a continuous crystalline line. Growth of the line from the formed crystal seed could be realized starting from 8 kHz repetition rate but only at 25 kHz or higher repetition rate we were able to obtain a homogeneous line. Too high average power also affected homogeneity. For example, at pulse repetition rate of 25 kHz homogeneous crystalline line could be grown at the speed range of 5-8 $\mu\text{m/s}$ and average power range of 0.45-0.75 W. We also studied dependence of the width of crystalline lines and homogeneity on the beam scanning speed and the average laser power at constant repetition rate. At 100 kHz repetition rate and 1.31 W average laser power, scanning speed below 40 $\mu\text{m/s}$ did not enable writing of homogenous line, the crystals growing separately and disoriented, which is confirmed by optical microscopy (Fig. 4). The scanning speed above 50 $\mu\text{m/s}$, does not result in crystal line formation and refractive index modification is only observed by optical microscopy whereas smoother lines could be obtained in 40-50 $\mu\text{m/s}$ speed range (Fig. 5).

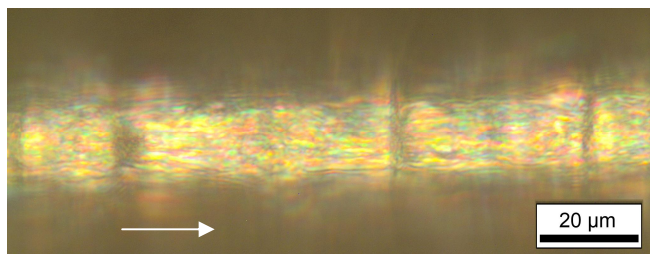


Figure 4. Optical micrograph of crystal lines written under average power $P=1.3$ W and scanning speed 22 $\mu\text{m/s}$ viewed through crossed polarizers. An arrow indicates laser scanning direction

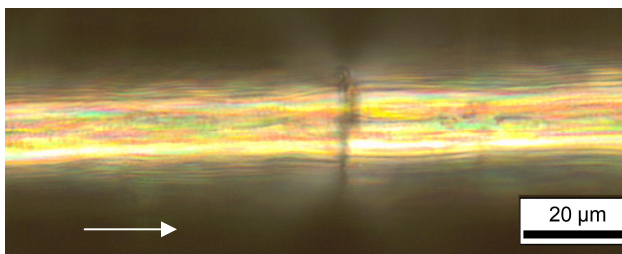


Figure 5. Optical micrographs of crystal lines written under average power $P=1.3$ W and scanning speed 45 $\mu\text{m/s}$ viewed through crossed polarizers. An arrow indicates the laser scanning direction

At the same time, scanning with the speed higher than 5 $\mu\text{m/s}$ results in formation of crystal lines with the practically constant width (Fig. 6). For the scanning speed below 5 $\mu\text{m/s}$, samples cracking is observed and crystalline regions increase in size.

The crystal line width linearly depends on the average power of the laser beam in the wide power range under conditions of constant scanning speed and pulse repetition rate (Fig. 7). This can be practically useful for gradual width control.

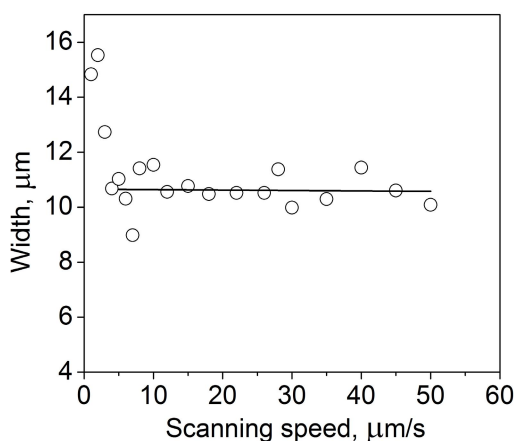


Figure 6. Dependence of width of crystalline lines on the scanning speed at constant average power ($P = 1.3$ W) and constant pulse repetition rate (100 kHz)

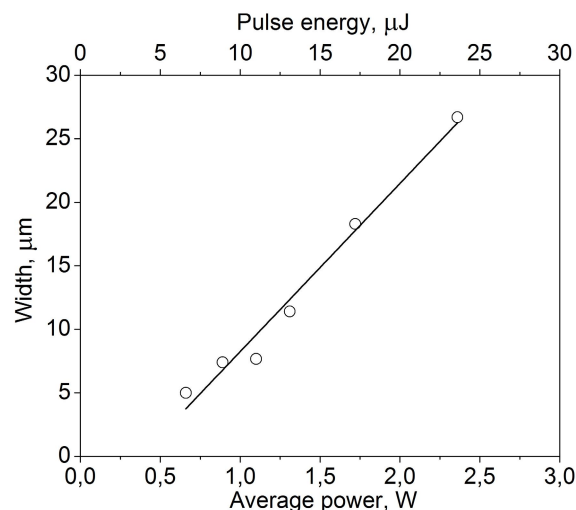


Figure 7. Dependence of width of crystalline lines on the average power at constant pulse repetition rate (100 kHz) and scanning speed ($U = 20$ $\mu\text{m/s}$)

The crystalline lines were investigated by micro-Raman spectroscopy which allowed us certain identifying this crystalline phase as LaBGeO_5 (Fig. 8) since the detected narrow Raman bands of the crystallized area fully corresponded to data reported for LaBGeO_5 single^[32] or powdered^[33] crystal.

To find out possible orientation of c-axis, polarized Raman spectra was recorded for excitation beam with polarization parallel and perpendicular to direction of the line (Fig. 9). In the smooth lines obtained at 25 kHz or higher repetition rate these spectra showed good reproducibility in different points of the line and matched back-scattering Raman spectra registered for excitation polarization parallel and perpendicular to c-axis of LaBGeO₅ single crystal^[32]. This confirmed that c-axis is oriented along the line growth direction same to reported for this glass earlier^[16]. This also agrees to the spectrum registered at the cross-section (Fig. 8) of the line which well corresponds to the spectrum with excitation polarization perpendicular to c-axis, same to the spectrum (b) in Fig. 9.

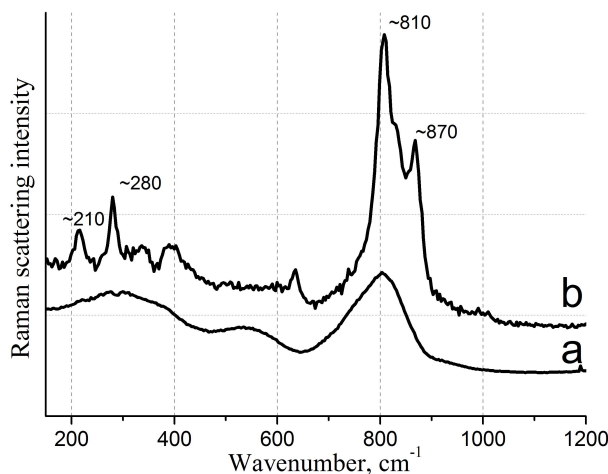


Figure 8. Raman spectra of: non-irradiated glass (a) and LaBGeO₅ crystalline line cross-section (b)

The most significant difference can be observed for the band at 390 cm⁻¹ which is much stronger when excitation polarization is parallel to the c-axis of the crystal. 2D Raman mapping of part of the crystalline line written at 25 kHz was carried for integral Raman scattering signal in 350-450 cm⁻¹ range including this peak (Fig. 10) and confirmed good homogeneity of the crystal structure orientation within this part.

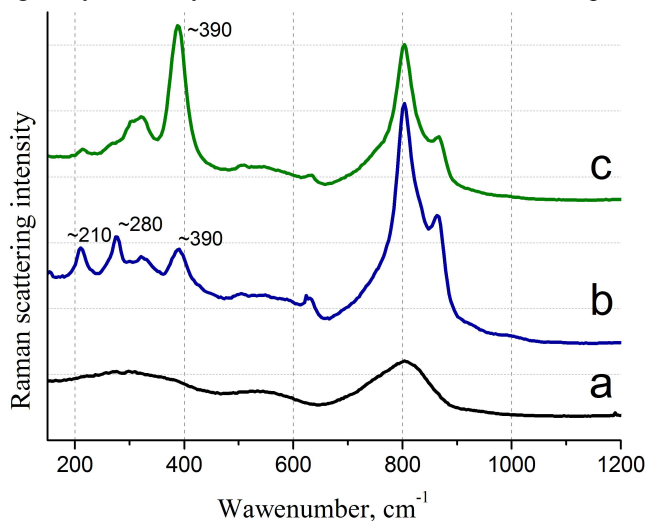


Figure 9. Polarized Raman spectra of: non-irradiated glass (a), LaBGeO₅ crystalline line for Y(XX)Y (b) and Y(ZZ)Y (c) geometry

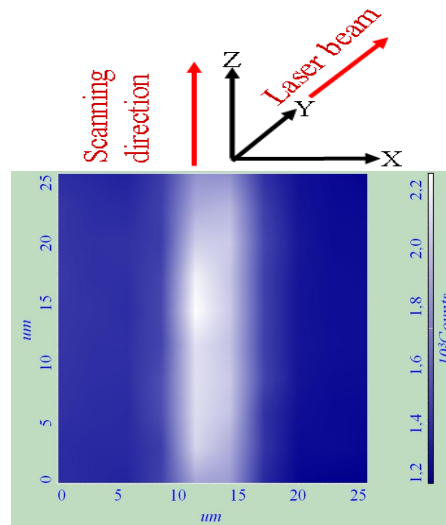


Figure 10. 2D map for integral Raman signal within 350-450 cm⁻¹ in Y(ZZ)Y geometry

Importantly, all the quantitative results reported in the present study are obtained for 100 μm and cannot be directly applied to other depths. Simple changing the focusing depth will change the shape of the cumulative heating region and the laser intensity profile due to aberration of the beam^[18] though it has been shown possible to compensate these effects using wavefront control^[19]. Homogeneity of the glass is also a crucial factor for fabrication of homogeneous highly oriented crystalline lines.

4. CONCLUSION

Femtosecond laser-induced growth of stillwellite-like LaBGeO_5 crystalline dots and continuous lines with c-axis oriented along the line direction are shown in $25\text{La}_2\text{O}_3 \cdot 25\text{B}_2\text{O}_3 \cdot 50\text{GeO}_2$ (mol.%) glass by means of femtosecond laser irradiation at different repetition rate below 100 kHz with lower boundary equal to 9 kHz for nucleation and microcrystal dots and 8 kHz for growth of lines from this dots. This is an order of magnitude as low as earlier reported lowest value required to obtain cumulative heating effect and more than 20 times as low as lowest repetition rate earlier reported for femtosecond laser-induced crystallization of oxide glasses. This value might be even lower if pulse energy higher than 110 μJ were available. Smooth homogeneous lines with oriented structure could be grown starting from 25 kHz whereas at 8-25 kHz their structure showed no homogeneity. Reverse exponential dependence of average time required for nucleation on the pulse repetition rate at constant average power of the laser beam was found out. Width of laser-written crystalline lines revealed independence on the writing speed in a certain speed range and nearly linear dependence on the pulse energy. These results open up opportunity for wider variation of femtosecond laser beam parameters for better control of space-selective growth of crystalline architectures in glasses.

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